SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE IN WATER

CHAY SIEW LENG

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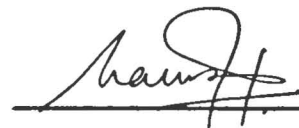
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   (PROF. MADYA DR. MARCUS JOPONY)

2. **EXAMINER 1**
   (DR. MD. LUTFOR RAHMAN)

3. **EXAMINER 2**
   (MR. MOH PAK YAN)

4. **DEAN**
   (PROF. MADYA DR. SHARIFF A.K. OMANG)

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ABSTRACT

Spectrophotometric analysis of phosphate according to ascorbic acid method has been studied. Absorbance measurement of phosphate was carried out at $\lambda = 880$ nm using UV-VIS spectrophotometer. For low phosphate concentrations (<1 µg/mL), a maximum absorbance value was obtained within 10 minutes after mixing of reagent while at higher concentrations, a maximum was not attained within 60 minutes. The relationship between absorbance and concentration was in accordance to the Beer-Lambert law for the phosphate concentration range 0-1 µg/mL while higher concentrations resulted a negative deviation from the Beer's law. The presence of chloride, nitrate, sulfate, nitrite, Ca^{2+} and Mg^{2+} ions in solution did not interfere in the phosphate analysis. By contrast, the presence of arsenate, silicate and Cr^{6+} ions interfered, particularly at higher concentrations.

ANALISIS SPEKTOFOTOMETRIK FOSFAT DALAM AIR

ABSTRAK

Analisis fosfat secara spektrofotometrik melalui kaedah asid askorbik telah dikaji. Nilai serapan adalah diukur pada panjang gelombang sebanyak 880 nm dengan menggunakan spektrofotometer UV-VIS. Bagi kepekatan fosfat yang cair, nilai serapan yang maksimum tercapai selepas 10 minit setelah reagen ditambahkan, tetapi tiada pencapaian nilai yang maksimum dalam tempoh masa selama 60 minit untuk kepekatan fosfat yang tinggi. Hubungan antara nilai serapan dengan kepekatan adalah mematuhi hukum Beer-Lambert pada julat kepekatan 0-1 µg/mL. Sebaliknya sisihan negatif daripada hukum Beer berlaku pada kepekatan yang lebih tinggi daripada 1 µg/mL. Kehadiran ion klorida, ion nitrat, ion sulfat, ion nitrit, Ca^{2+} dan Mg^{2+} dalam larutan tidak memberi kesan terhadap nilai serapan fosfat. Sebaliknya, kehadiran ion arsenik, ion silikat dan Cr^{6+} mengganggu nilai serapan fosfat terutama pada kepekatan ion yang tinggi.

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LIST OF SYMBOLS

UV-VIS	ultraviolet-visible
T	transmittance
I_0	initial intensity of radiation entering
I	light intensity
b	optical path length
c	concentration of sample (mol/L)
A	absorbance
E	molar absorptivity coefficient at the specified wavelength (M/cm)
λ	wavelength
M_x	concentration of solution
V	volume of solution
t	time

CHAPTER 1

INTRODUCTION

1.1   CONTEXT AND RELEVANCE OF STUDY

Phosphorus in water typically exists as orthophosphates namely HPO_4^{2-}, $H_2PO_4^-$ and PO_4^{3-} (Holtan et al., 1988). Excessive phosphate in surface water as a result of anthropogenic inputs is known to cause eutrophication (Zeng et al., 2004). Therefore, phosphate is an important water quality parameter in water and wastewater analysis (Petruzzelli et al., 2003). The methods of phosphate analysis include gravimetric method (Broberg and Pettersson, 1988; Norwitz et al., 1971), ion exclusion chromatography method (Karmarkar, 1999; Zeng et al., 2004) and spectrophotometric or colorimetric method (APHA, 1995).

Colorimetrically, phosphate in water can be determined according to several methods namely vanadate method, stannous chloride method and ascorbic acid method (APHA, 1995). Basically, these methods involve the addition of a reagent to a solution or sample containing phosphate. The intensity of the resultant colored complex is measured at a specific wavelength (λ). According to the Beer-Lambert law, the intensity (absorbance) is proportional to concentration of the analyte (Shugar and Ballinger, 1996).

Colorimetric analysis, however, can be subjected to positive or negative interferences by other anions or cations which are present in the solution (Vogel, 1978). These interfering ions can affect complex formation as well as color intensity, depending on the type of ion and its concentration. Also, the formation and stability of the complex is time-dependent. Thus, the absorbance measurements need to be determined at a specific time (APHA, 1995).

1.2   OBJECTIVES OF STUDY

The objectives of this study are:

(i)   To determine the effect of reaction time on the intensity (absorbance) of colored complex during colorimetric analysis of phosphate according to ascorbic acid method.

(ii)   To evaluate the relationship between concentration and absorbance.

(iii)   To determine the effect of anion type and its concentration on colorimetric analysis of phosphate according to ascorbic acid method.

(iv)   To determine the effect of cation type and its concentration on colorimetric analysis according to ascorbic acid method.

1.3   SCOPE OF STUDY

This study will focus on colorimetric analysis of phosphate according to the ascorbic acid method. Absorbance measurement at $\lambda = 880$ nm will be carried out in the presence or absence of other anions and cations in solution. The anions to be investigated include chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), nitrite (NO_2^-), silicate (SiO_3^{2-}) and arsenate (AsO_4^{3-}) while the cations are calcium(II), Ca^{2+}, magnesium(II), Mg^{2+} and chromium(VI), Cr^{6+}. The effect of the ions will be evaluated at varying concentration. Absorbance measurements will also be carried out at different time intervals following the mixing of the analyte and reagent.

CHAPTER 2

LITERATURE REVIEW

2.1 PHOSPHATE IN WATER

2.1.1 Forms and Distribution of Phosphate

Phosphorus is an essential nutrient for terrestrial and aquatic plants (Kim *et al.*, 2003). Phosphorus occurs in natural water and in wastewaters bound to oxygen almost solely as phosphates. It comprises of orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. It occurs in solution, in particles or detritus, or in the bodies of aquatic organisms (APHA, 1995). Phosphates come from a variety of sources including agricultural fertilizers, domestic wastewater, detergents, industrial wastes and geological formations (Holtan *et al.*, 1988).

The distribution of the different species of orthophosphate is pH-dependent (Roques, 1996). $H_2PO_4^-$ is the predominant species in the pH range 4-6 while at pH >8, HPO_4^{2-} is the major species present (Figure 2.1).
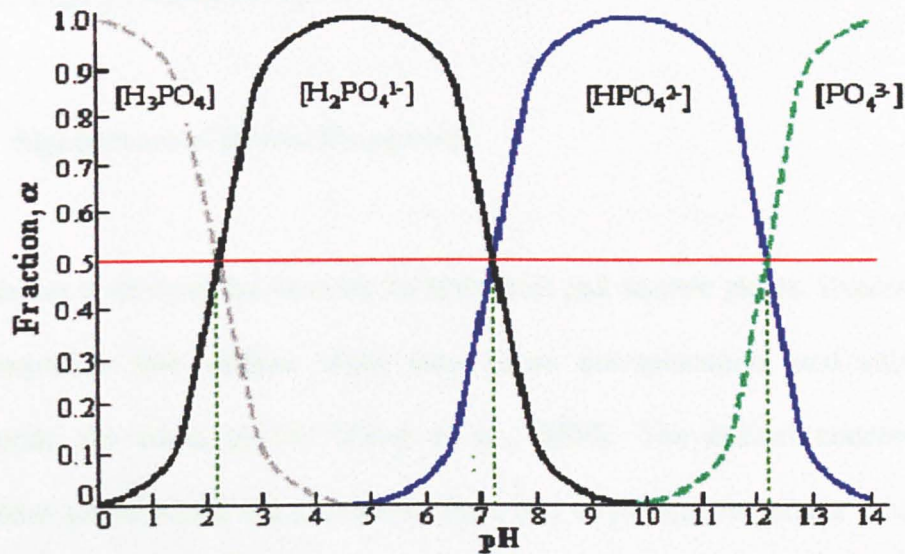
Figure 2.1 Distribution of phosphate species with pH.

2.1.2 Concentration of Phosphate

Phosphorus generally occurs in traces in natural waters (Nebergall, 1971). Natural waters mostly contain total phosphorus compounds at concentrations of less than 0.1 mg/L (Rump and Krist, 1992), while the natural levels of orthophosphate usually range from 0.005 to 0.05 mg/L (Nebergall, 1971). Although inorganic phosphorus are not toxic, they are undesirable components of rivers and lakes used as sources as raw water for drinking water preparation owing to the danger of eutrophication. Long-term eutrophication will usually be prevented if total phosphorus levels and orthophosphate levels are below 0.5 mg/L and 0.05 mg/L, respectively (Rump and Krist, 1992).

Phosphate is usually found in large concentration in raw or treated sewages, agricultural drainages, and industrial effluents (Nebergall, 1971). For example, the

total amount of phosphate present in municipal wastewaters is typically of the order of 10 to 25 mg/L (Roques, 1996).

2.1.3 Significance of Excess Phosphate

Phosphorus is an essential nutrient for terrestrial and aquatic plants. Excessive inputs of phosphorus into surface water may cause eutrophication, and subsequently, deteriorate the water quality (Zeng *et al.*, 2004). The critical concentration of phosphate above which the growth of algae and other aqueous plants accelerates, is 0.01 mg/L for dissolved phosphate and 0.02 mg/L for total phosphate (Kim *et al.*, 2003).

Eutrophication is the process by which a body of water undergoes an increase in the concentration of chemical elements required for living things, for example, phosphorus (Vitousek, 1996). Increased nutrient loading may lead to a population explosion of photosynthetic algae and blue-green bacteria that become so thick that light cannot penetrate the water (Campbell, 1999). Bacteria deprived of light beneath the surface die, and as they decompose, dissolved oxygen in the water is lowered and eventually a fish kill may result (Botkin and Keller, 2003).

2.2 METHODS OF PHOSPHATE ANALYSIS IN WATER

The determination of phosphate in natural samples is important in environmental chemistry and geochemistry, hence it is desirable to have available sensitive and accurate methods for phosphate analysis. There are several methods used to determine

phosphate in water, including gravimetric method (Broberg and Pettersson, 1988; Norwitz et al., 1971), ion exclusion chromatography method (Zeng et al., 2004) and spectrophotometric or colorimetric method (APHA, 1995).

In gravimetric analysis, the analyte being determined is converted into an insoluble precipitate which is collected dried and weighed (Vogel, 1978). In the case of phosphate, this analyte is precipitated as magnesium ammonium phosphate hexahydrate, $Mg(NH_4)PO_4.6H_2O$ using $MgCl_2.NH_4Cl$ as precipitating agent (Harris, 1991; Hikime et al., 1973). Because the weight of the precipitate can be measured accurately, gravimetric method is an accurate and precise method for analysis of phosphate (Christian, 2004).

Ion chromatography (IC) is one of the techniques for determinations of anions in water (Karmarkar, 1999; Zeng et al., 2004). The basic concept of IC is that the sample is eluted through an anion exchanger inside a column. The anions of interest are separated on the basis of their relative affinities for the anion exchanger. The separate anions are subsequently analyzed quantitatively. For the determination of orthophosphate, the absorbance of the reduced 12-molybdophosphoric acid is monitored at 660 nm (Spivakov et al., 1990). Ion chromatography has a relatively high detection limit (0.1 mg/L) and cannot be used for sample with high concentration of interfering anions without sample pretreatment (D' Angelo et al., 2001).

Comparatively, the most widely used method for phosphate analysis is the spectrophotometric method.

2.3 SPECTROPHOTOMETRIC OR COLORIMETRIC ANALYSIS

2.3.1 Basic Concepts

The variation of the color of a system with change in concentration of some component forms the basis of what the chemists commonly terms colorimetric analysis (Vogel, 1978). This analysis generally involves the addition of a reagent to a solution or sample containing an analyte. The intensity of the resultant colored complex is subsequently measured at a specific wavelength, λ (Nebergall, 1971). According to the Beer-Lambert law, the intensity of such color is proportional to the concentration of the analyte (Shugar and Ballinger, 1996). It means that quantitatively the amount of radiation absorbed (the absorbance) at an appropriate wavelength is proportional to the concentration of light-absorbing chemical in sample. Since absorption occurs fast, spectrophotometric method is a very fast and convenient method of quantitative analysis (Black, 1965; Fritz and Schenk, 1987).

2.3.2 Instrumentation

The principal instrument used in colorimetric analysis is a spectrophotometer. Typically, a spectrophotometer comprised of 5 main components namely light source, monochromator, sample cell or curvet, a detector or transducer and read out device (Figure 2.2).
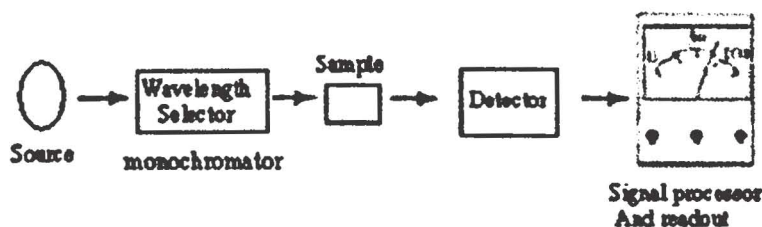
Figure 2.2 Components of instruments for optical spectrophotometry (Silberberg, 2003).

The light passes through a slit and dispersed along a monochromator. The monochromator then select a beam of monochromatic radiation to illuminate the sample in a curvet. The light that passes through the sample cell reaches the detector, which records the intensity of the transmitted light. The absorbance or intensity readings are displayed by the readout device, which is typically a computer system equipped with a printer (Pavia *et al.*, 2001; Skoog *et al.*, 2004).

a. **Light Source**

The light source produces the polychromatic light used to illuminate the sample (Harris, 1991). The type of light source determines the wavelength of the polychromatic light. A tungsten filament lamp produces radiation in the range 320-2500 nm, covering the entire visible region and parts of the infrared and ultraviolet regions. By contrast, a deuterium lamp produced light in the UV range at 200-400 nm (Figure 2.3).
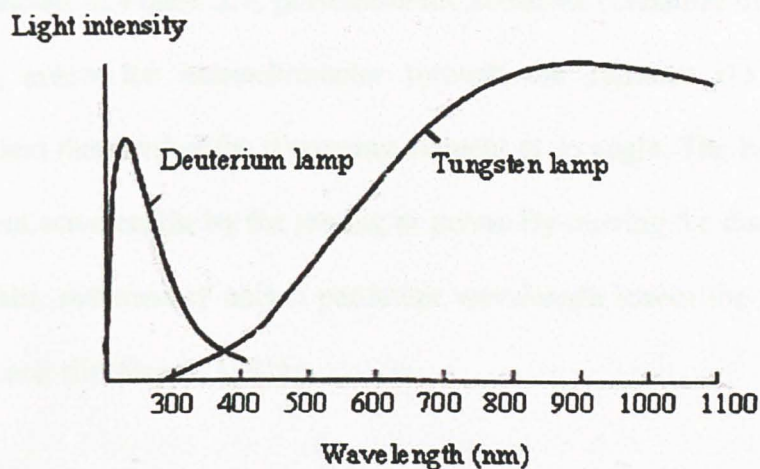
Figure 2.3 Intensity and wavelength region of a tungsten filament and a deuterium arc lamp.

b.   Monochromator

The function of a monochromator is to select a beam of monochromatic (one wavelength) radiation to illuminate the sample. A monochromator consist of an entrance slit, a collimating lens, a dispersing device, usually a prism or a grating, a focusing lens, a dispersing device and an exit slit (Fritz and Schenk, 1987).
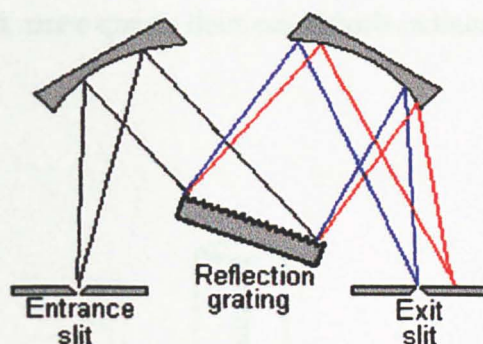
Figure 2.4 Diagram of Czerney-Turner grating monochromator.

As shown in Figure 2.4, polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit (Harris, 1991).

c.   Sample cell

The cell (Figure 2.5) for the sample and reference solution must be transparent to the radiation which will pass through them in the wavelength region being measured. The cells for use in visible and ultraviolet spectrophotometer are usually curvets into 1cm path length (Christian, 2004). Cells used in the visible region are made of optical quality borosilicate glass and plastic that can be used down to about 320nm, at which point the glass begins to absorb most of radiant energy (Fritz and Schenk 1987). For measurement in the ultraviolet region of the spectrum, however, glass and plastic can not be used because they absorb ultraviolet radiation. Instead, cells made of quartz or other silica must be used, since quartz does not absorb radiation in this region (Shugar and Ballinger, 1996).

Figure 2.5 An example of sample cell.

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APPENDIX A

Preparation of Anions Stock Solution

a. **Stock Chloride Solution**

Stock chloride solution 500 µg/mL was prepared by dissolving 824.0 mg sodium chloride, NaCl in distilled water and diluting to 1000mL.

b. **Stock Nitrate Solution**

Stock nitrate solution 100 µg/mL was prepared by dissolving 0.7218 g potassium nitrate, KNO_3 in distilled water and diluting to 1000 mL.

c. **Stock Sulfate Solution**

Stock sulfate solution 100 µg/mL was prepared by dissolving 0.1479 g anhydrous sodium sulfate, Na_2SO_4 in distilled water and diluting to 1000 mL.

d. **Stock Silicate Solution**

Stock silicate solution 500 µg/mL was prepared by dissolving 1.76 g sodium pentahydrate, $Na_2SiO_3 \cdot 5H_2O$ in distilled water and diluting to 1000 mL.